Understanding Mercury Chemistry in the Flue Gas Using Experimental and Quantum Modeling Studies

Xihua Chen[1], Huiying Zhu[2], Wei Sun[1], Joseph R. Flora[2], Eric Borguet[3] and Radisav Vidic[1]

[1] Department of Civil and Environmental Engineering, University of Pittsburgh, Pittsburgh, PA 15261

[2] Department of Civil and Environmental Engineering, University of South Carolina, Columbia, SC 29208

[3] Department of Chemistry, Temple University, Philadelphia, PA 19122

ABSTRACT

The impact of fly ash composition and flue gas components on mercury speciation were evaluated in this study. Experimental studies revealed that the unburned carbon was the most important fly ash component influencing mercury speciation. Quantum modeling was used to investigate Hg adsorption and oxidation on carbon surfaces in the presence of HCl, NO_2 or SO_2. NO_2 and HCl promoted mercury oxidation and adsorption on carbon black. Quantum modeling support experimental findings in the case of NO_2 and SO_2 impact while the impact of HCl could not be explained with modeling work. An equilibrium model for Hg, HCl and carbon black system was setup and this model indicated that surface reactions are kinetically controlled.

BACKGROUND

Many studies showed that Hg speciation in coal fired power plants is related to flue gas and fly ash composition. This study evaluated simultaneous impact of fly ash and flue gas composition on mercury speciation under relevant process conditions. Quantum modeling methods were used to study homogeneous mercury oxidation mechanisms. However, reports of heterogeneous mercury reactions are quite limited. Padak et al. modeled Hg adsorption on carbon with a 16 carbon model and concluded the attachment of Cl and O functional groups on carbon surfaces improves Hg

METHODS

Experimental Methods

SEM-EDAX, XPS, TPD, LOI, BET, Particle Size Distribution tests were applied to analyze six fly ash samples (Table 2). All samples were tested for mercury uptake at 140 ºC in a fixed bed system using the simulated flue gas composition given in Table 1.

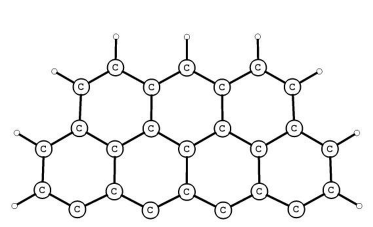
Table 1. Simulated Flue gas composition

Gas	CO_2	O_2	NO	NO_2	HCl	SO_2	N_2
Concentration	13.5%	6%	300 ppm	20 ppm	50 ppm	0.15%	Balance

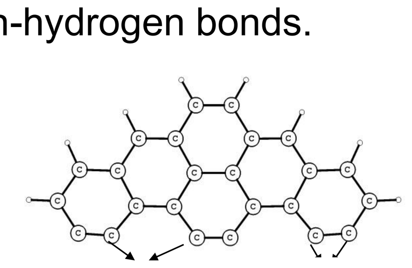
Breakthrough experiments were conducted using influent elemental mercury concentration of 18μg/m³ and a fixed bed reactor charged with 50 mg of sample mixed with 4 g glass beads

Quantum Modeling

Carbon black was modeled as a graphite layer with several benzene rings. Two types of edges were cut from the graphite layer and the broken carbon-carbon bonds were substituted with carbon-hydrogen bonds.



Zigzag model



Armchair model

Gaussian 03 and PC-GAMESS 7.0 was used in the calculations. The adsorption of gas phase components on both zigzag edge model and armchair model were studied.

RESULTS

Fly ash sample characterization

Table 2 shows that SH fly ash has the highest LOI value, highest amount of unburned carbon and largest particle size. Its SEM image (Figure 3) shows relatively high amount of soot, which accounts for the high surface area and high LOI.

Table 2. Fly ash characteristics

Sample	LOI(%)	Surface Area (m^2/g)	Moisture (%)	Particle size (μm)
SH	37.2	17.9	0.1	92.7
Brayton	18.1	5.8	0.1	77.6
Gaston	11.9	2.1	0.2	30.3
PP	1.0	3.0	0.2	48.0
CE1	6.0	2.5	0.1	32.7
CE2	3.1	1.1	0.1	23.4

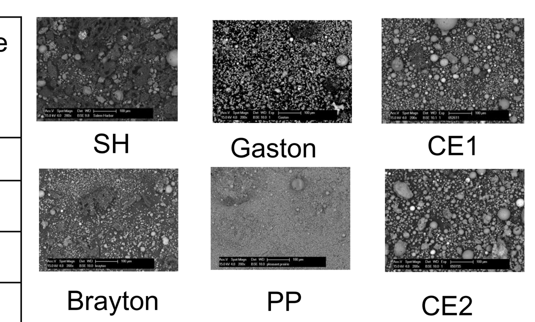


Figure 3. SEM image of fly ash samples

Mercury uptake by fly ash samples

Six fly ash samples were tested for mercury uptake. Results for SH fly ash are shown in Figures 4. Table 3 shows the summary of all test with selected fly ash samples.

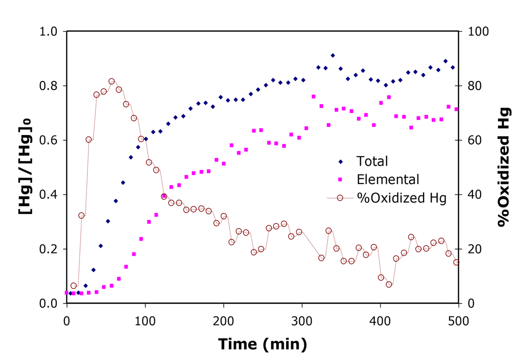


Figure 4. Hg uptake test with 50 mg SH fly ash at 140°C

Table 3. Hg uptake and oxidation after four-hour exposure

Sample	Mercury Load (mg/g)	Oxidizeg %
SH	47.9	22.9%
Brayton	38.3	9.3%
Gaston	14.6	7.3%
PP	8.8	8.1%
CE1	13.1	1.6%
CE2	13.2	5.2%

The results also indicated that LOI and surface area are correlated with the ability of fly ash to oxidize mercury.

Effect of pure components in fly ash on Hg speciation

Breakthrough tests showed that pure Al_2O_3, MgO, CaO, TiO_2 (anatase) and SiO_2 do not adsorb or oxidize elemental Hg in simulated flue gas. Fe_2O_3 and carbon black (Figure 5) showed significant oxidation and uptake of mercury.

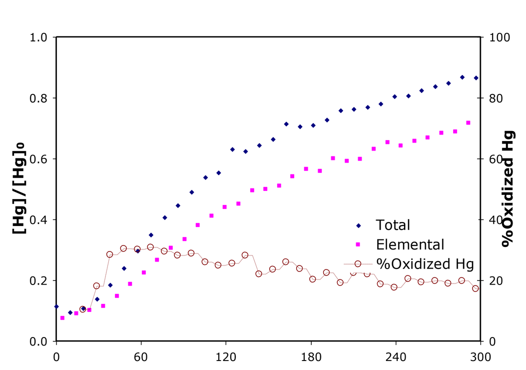


Figure 5. Hg uptake test with 50 mg Carbon Black at 140°C

The presence of Fe_2O_3 in fly ash samples is limited to about 1%. On the other hand, unburned carbon constitutes as much as 30% of fly ash and it is the largest contributor to mercury oxidation by fly ash samples

Effect of flue gas composition on Hg uptake by Carbon Black

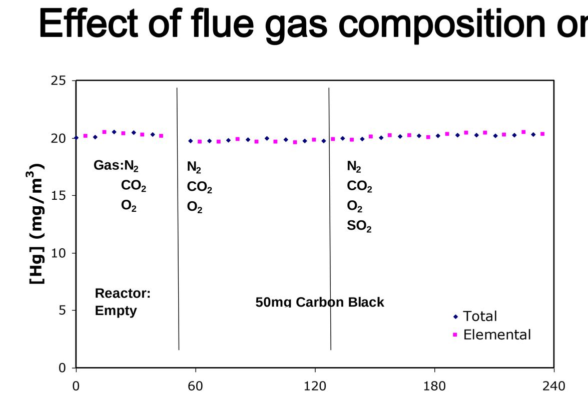


Figure 6. Effect of SO_2 on mercury uptake by Carbon black in N_2+CO_2+O_2 at 140°C

Breakthrough studies showed that N_2,CO_2,O_2 and SO_2 (alone or in combination) can not cause any effect on mercury uptake and oxidation by carbon black.

NO_2 did promote mercury oxidation both in nitrogen gas and in the presence of CO_2 and O_2 (Figures 7 and 8).

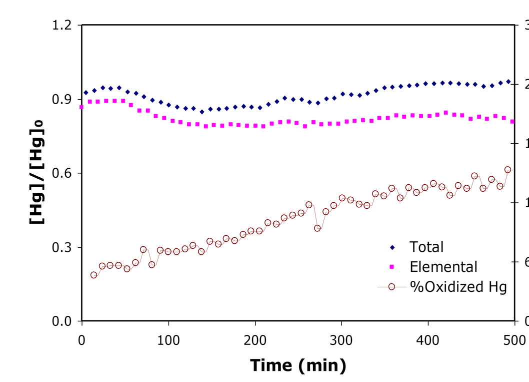


Figure 7. Effect of NO_2 on mercury uptake by carbon black in N_2

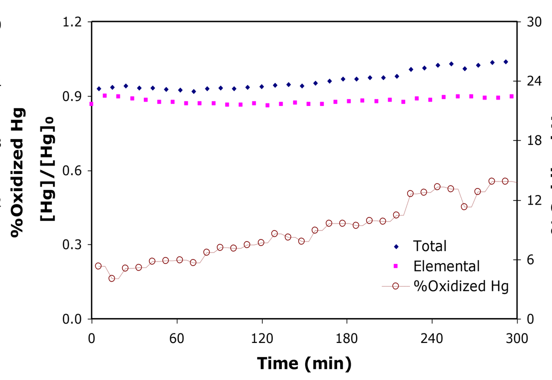


Figure 8. Effect of NO_2 on mercury uptake by carbon black in N_2+CO_2+O_2

HCl showed the most pronounced impact on mercury oxidation by carbon black (Figure 9). Addition of O_2 significantly improved mercury capture and oxidation (Figure 10). Results on Figure 10 suggest that the carbon surface was catalyzing oxidation of mercury with subsequent adsorption of Hg^{2+}.

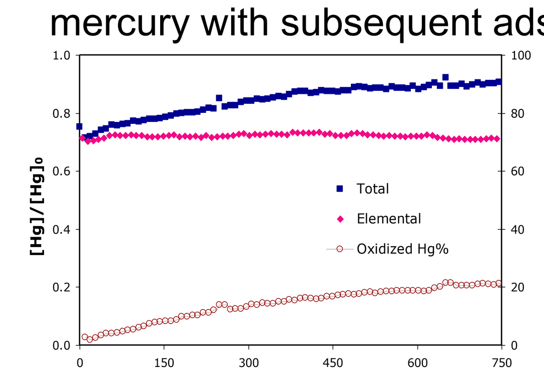


Figure 9. Effect of HCl on mercury uptake by carbon black in N_2

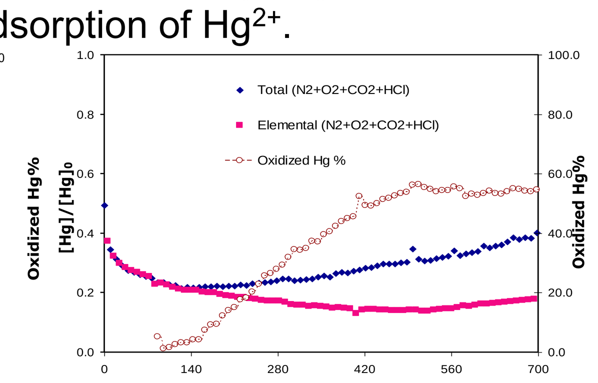
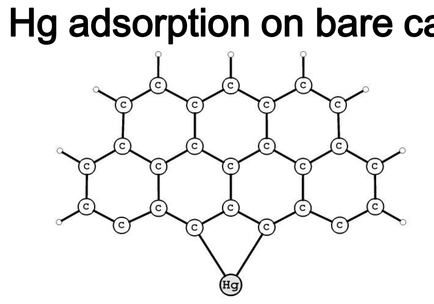


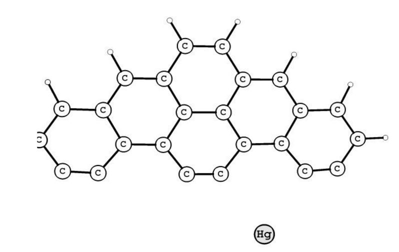
Figure 10. Effect of HCl on mercury uptake by carbon black in N_2+CO_2+O_2

Quantum modeling: Impact of SO_2, NO_2 and HCl Attachment on Mercury Capture

Hg adsorption on bare carbon



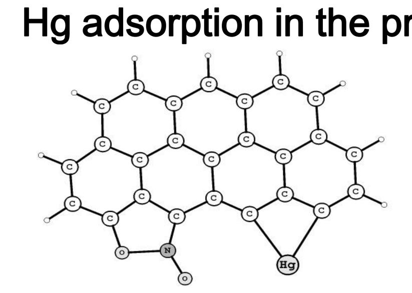
Binding Energy: -9.1 kcal/mol



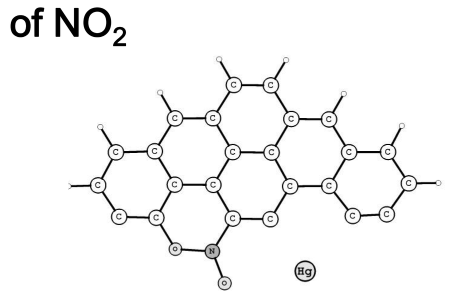
Binding Energy: -4.0 kcal/mol

Mercury binding energies on both carbon models are low, indicating that Hg^0 adsorption on carbon black is unlikely to happen.

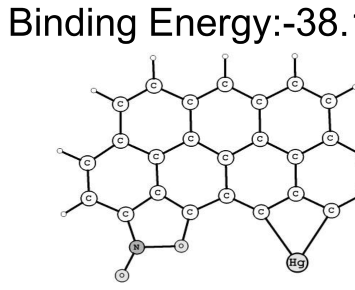
Hg adsorption in the presence of NO_2



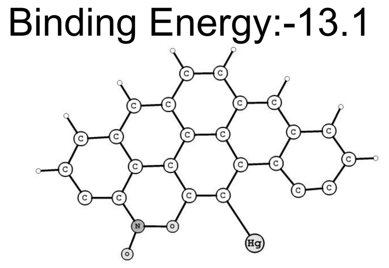
Binding Energy:-38.1 kcal/mol



Binding Energy:-13.1 kcal/mol



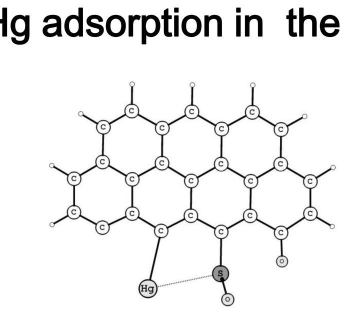
Binding Energy:-37.6 kcal/mol



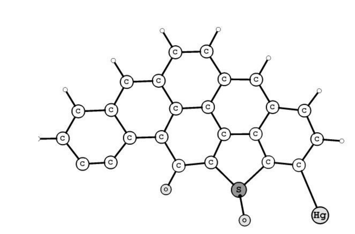
Binding Energy:-13.2 kcal/mol

This result shows the mercury binding energy is higher and it would explain the observed Hg removal in packed bed experiments with NO_2 and N_2 in the gas stream.

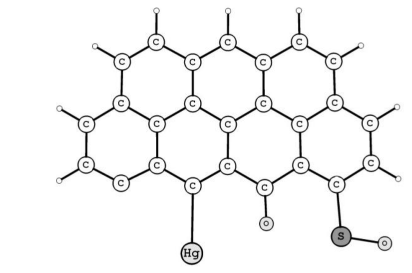
Hg adsorption in the presence of SO_2



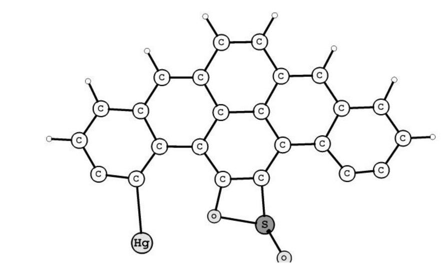
Binding Energy:-3.4 kcal/mol



Binding Energy:-10.8 kcal/mol



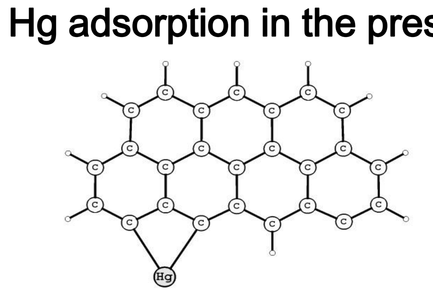
Binding Energy:-11.7 kcal/mol



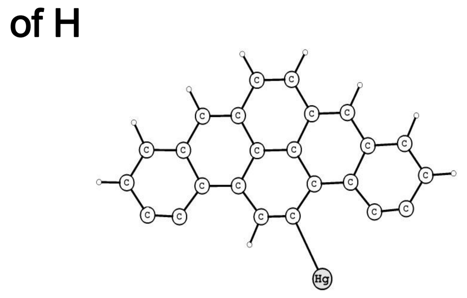
Binding Energy:-13.7 kcal/mol

From binding energy calculation above, SO_2 will not enhance adsorption of Hg on carbon surface.

Hg adsorption in the presence of H

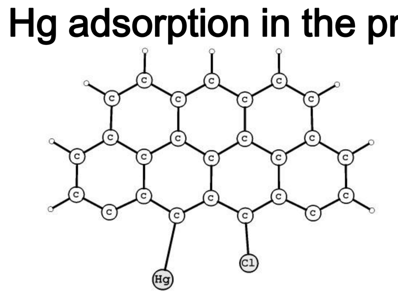


Binding Energy: -3.3 kcal/mol

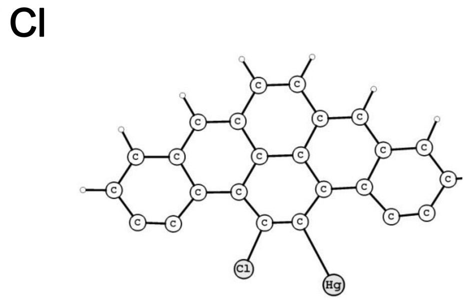


Binding Energy: -10.6 kcal/mol

Hg adsorption in the presence of Cl



Binding Energy: -3.3 kcal/mol



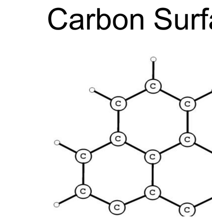
Binding Energy: -10.6 kcal/mol

Both mercury adsorption and oxidation occur in HCl and N_2 stream in experimental Hg uptake tests, which can not be explained by binding energies calculation.

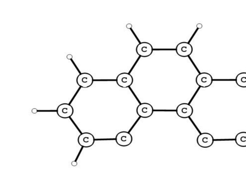
Equilibrium model for Hg, HCl and carbon black system

Gas phase: H atom, H2, Cl atom, Cl2, HCl, Hg, HgCl, HgCl2

Carbon Surface

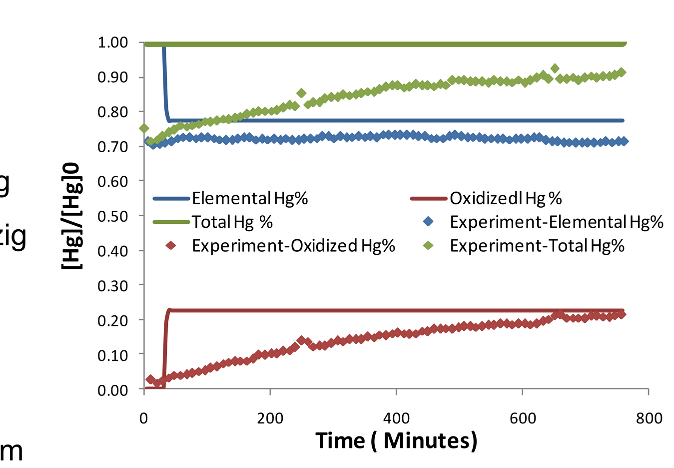


Zigzag Carbon Site



Armchair Carbon Site

H-Czig, Cl-Czig, Hg-Czig, HgCl-Czig, HgCl2-Czig, H-Carm, Cl-Carm, Hg-Carm, HgCl-Carm, HgCl2-Carm



Model Results vs Experimental results of Hg Uptake in HCl and Carbon Black Systemc

Results are calculated with the assumption that 40% of the carbon surface are zigzag carbon sites. Model results can fit experimental results when the system approaches equilibrium. This model shows no oxidation and adsorption at the very beginning, after which mercury oxidation happens immediately. This does not agree with experimental results. Therefore, surface reactions are likely to be kinetically controlled.

CONCLUSIONS

1. Increase in LOI and surface area resulted in an increases in Hg adsorption and oxidation. Fe_2O_3 and carbon black promote Hg adsorption and oxidation. Unburned carbon is the most important fly ash component influencing Hg speciation. HCl and NO_2 promote Hg adsorption and oxidation on carbon black in N_2. Oxygen plays an important role in Hg adsorption and oxidation in the presence of HCl.
2. Quantum modeling work shows consistency with experimental results in the presence of NO_2 and SO_2 while there is no agreement for the impact of HCl. An equilibrium model for Hg, HCl and carbon black system was setup and this model indicated that surface reactions are kinetically controlled.

Acknowledgment

This study is supported by the US Department of Energy under the Contract No. DE-FG26-05NT42534